

# Beauty and the Beast

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# Beauty and the Beast



# A Comparison of Trivalent and Hexavalent Black Chromium Plating Processes

**“The Beauty”**



Chromium Sulfate-based  
Trivalent Black Chromium

**“The Beast”**



Chromium Trioxide-based Hexavalent  
Black Chromium

# Background:

- Hexavalent black chromium commercially available for over 50 years.
- Patents date back to 1952
- Gilbert and Buhman [1]
  - Developed process using chromic anhydride and acetic acid.
  - Artillery parts, rifle parts, and military equipment's at Rock Island Arsenal.
- Westinghouse Electric, Kewanee Oil (current day Atotech USA) were other pioneers to develop hexavalent black [2,3]

# Background:

- Trivalent black chromium patents date back to the early 1970s.
- Initial trivalent chromium patent: Gyllenspentz and Renton of Albright and Wilson [4-6]
  - Utilization of trivalent chromium with formate, acetate, bromide, and ammonia.
- Robert Tremmel [5-7]
  - Utilization of thiazole compounds.

# Operational Comparison

	Trivalent Black Chromium		Hexavalent Black Chromium
	Chloride	Sulfate	
Electrolyte metal component	Chromium Chloride	Chromium Sulfate	Chromium Trioxide
pH	2-3	3.2 - 3.8	<1
Temperature, F	70 - 120	120 - 140	90 - 120
Cathode Current Density, A/ft <sup>2</sup>	70 - 150	70 - 150	175 - 300
Anode-Cathode Ratio	2:1	2:1	1:1 - 3:1
Anode material	Carbon	Precious metal coated titanium	Lead-Tin (7%)
Rectifier voltage	Up to 12	Up to 12	4 - 12
Agitation	Mild air	Mild air	Optional
Maximum deposit thickness, microns	>1 $\mu\text{m}$	0.3 $\mu\text{m}$	>5 $\mu\text{m}$
Deposition rate, $\mu\text{m}/\text{min}$	0.15 - 0.25	0.02 - 0.03	0.1 - 0.18

Source: [3]

# Operational Comparison

## Trivalent Black

- Good throwing power
- Good covering power (similar to Watts nickel)
- Multiple chemical constituents need to be balanced for optimum black

## Hexavalent Black

- Poor throwing power
- Poor covering power (similar to bright hexavalent chromium)
  - May need auxiliary anodes to obtain good part coverage
- Fewer chemical components to balance

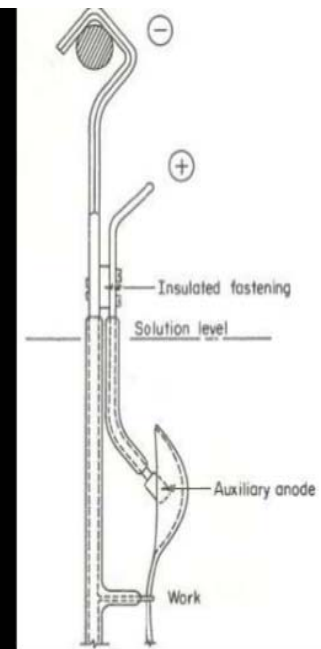


# Plating Rack Fixturing

## Trivalent Black chromium



## Hexavalent Black chromium



Integrated plating rack showing auxiliary anode for obtaining uniform coating thickness on a diecasting



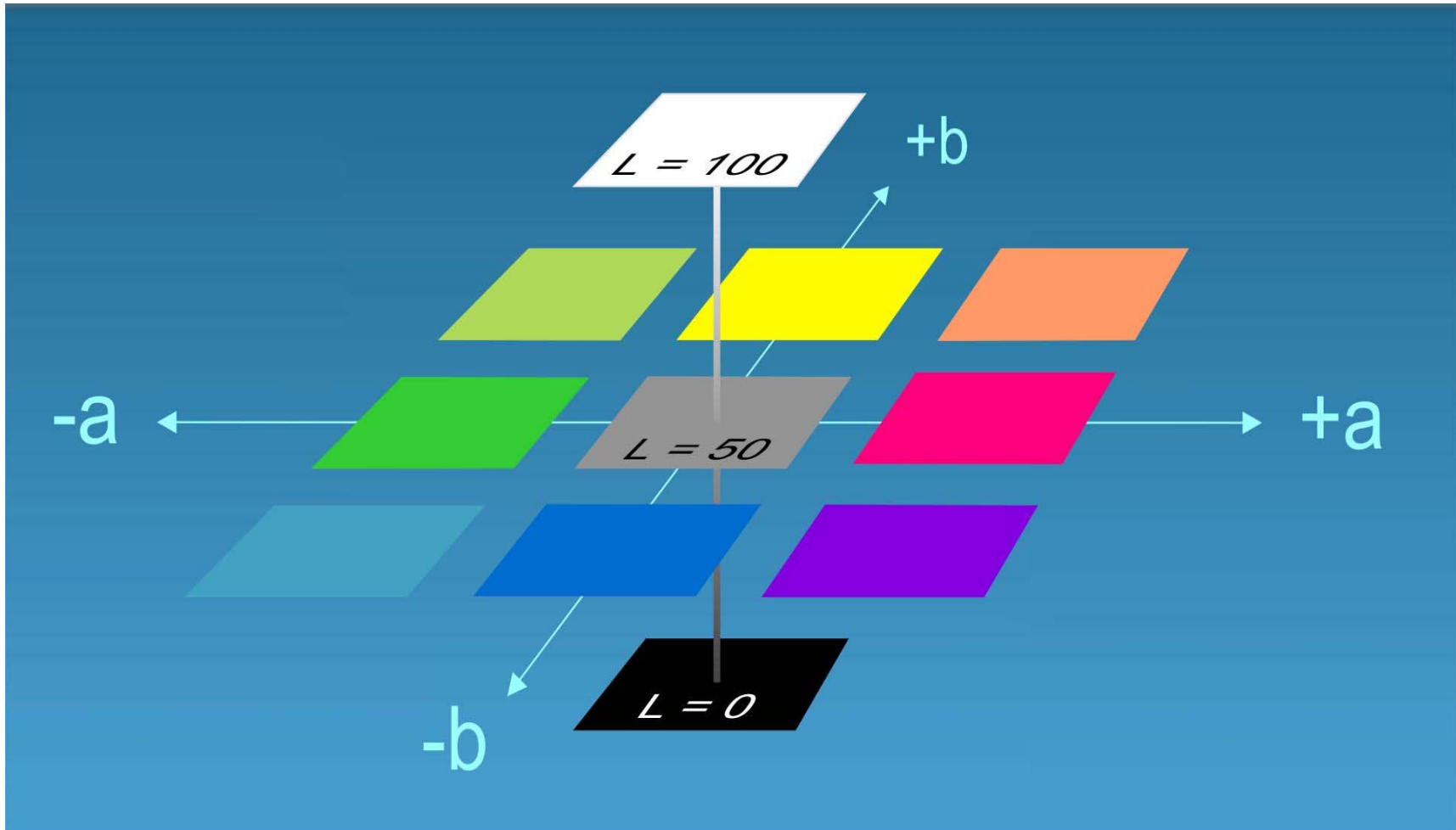
# How Black is Black?

Color can be measured with a colorimeter using LAB values for color and lightness.

Gloss meters can also be used to measure reflectivity.

Black can be a very specific term...

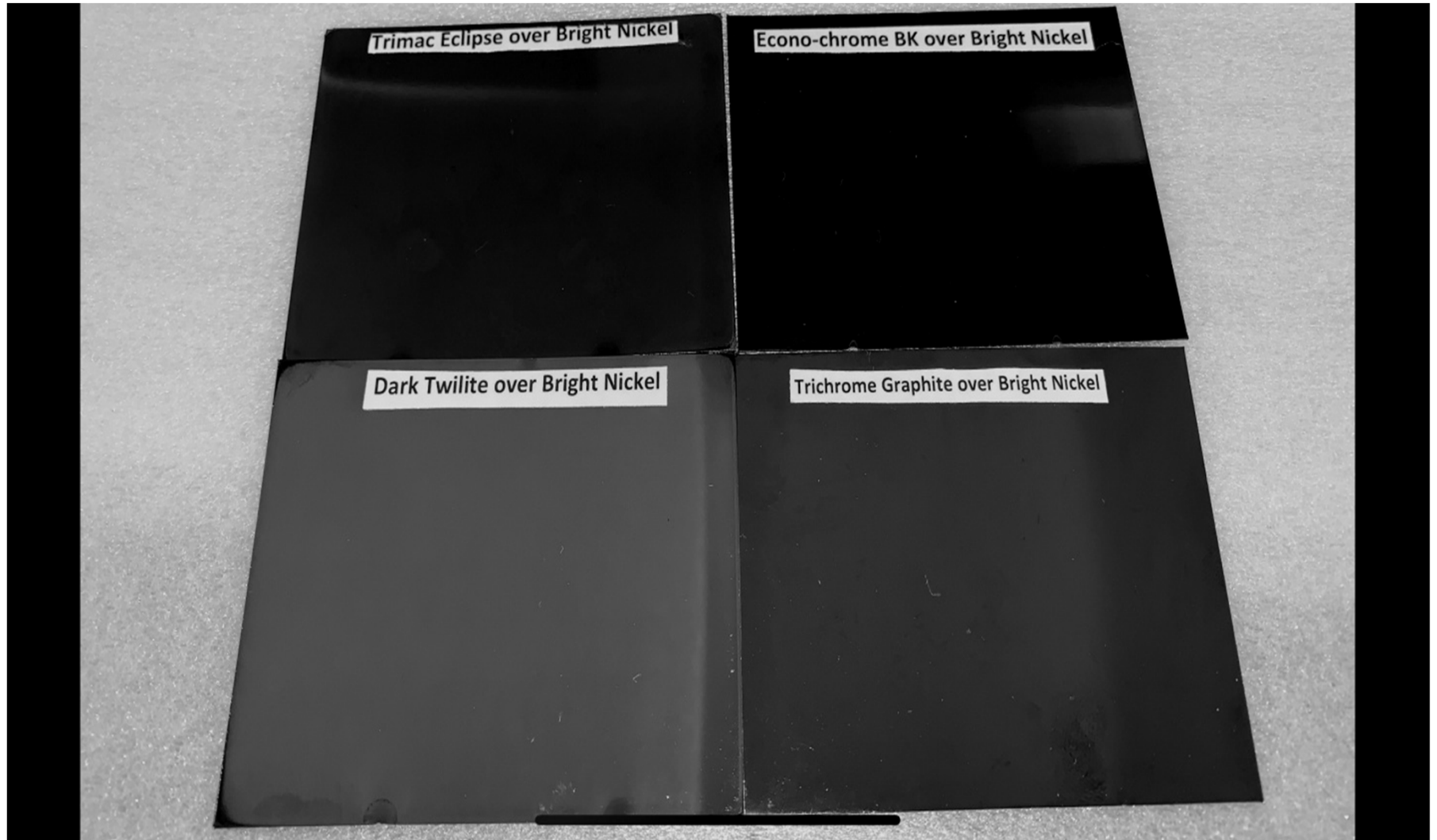
# Color



# L-A-B

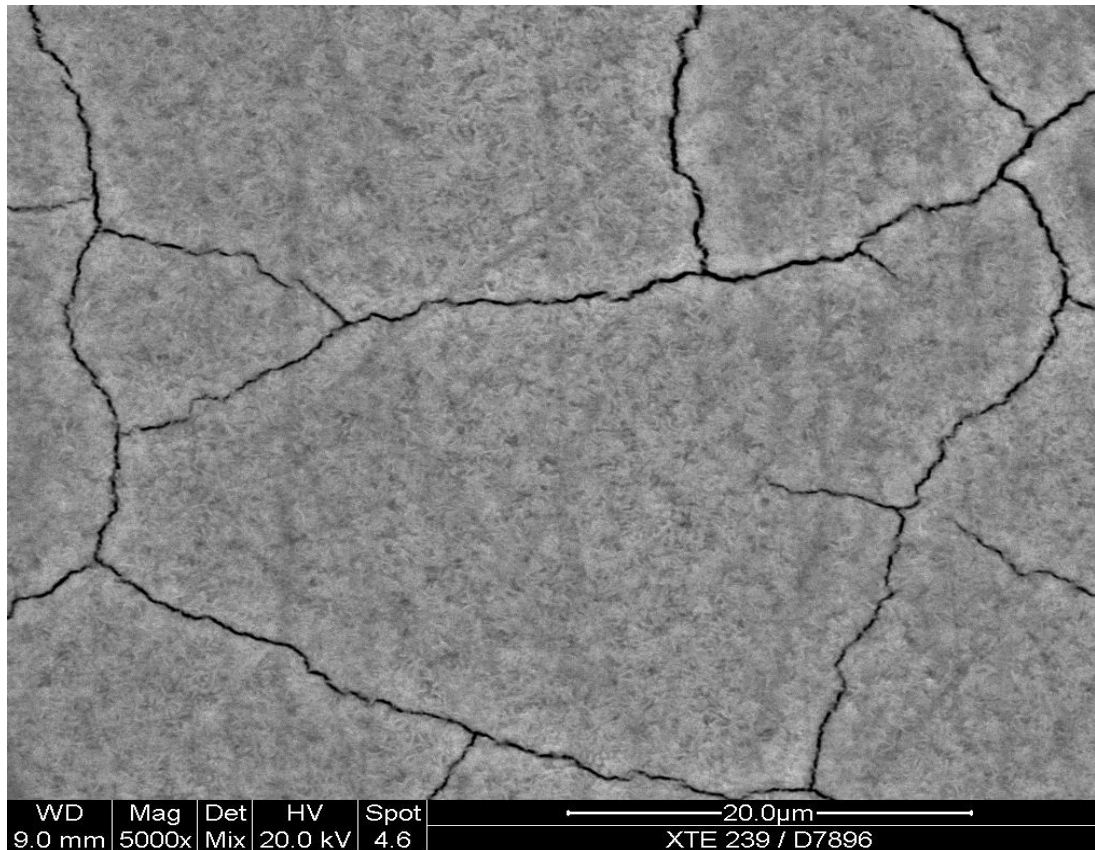
<b>Commercial Product</b>	<b>Supplier</b>	<b><u>L</u></b>	<b><u>A</u></b>	<b><u>B</u></b>
Trichromium Graphite	Atotech	68	1	6
Dark Twilight	MacDermid Enthone	81	1	4
Econo-chromium BK	Atotech	30	0	0
Econo-chromium BL plus oil	Atotech	33	1	1
Trimac Eclipse	MacDermid Enthone	50	2	5
Trichromium Graphite	MacDermid Enthone	67	2	6
Tristar 700 (chloride)	Coventya	54	0.1	4
Tristar 720 (Sulfate)	Coventya	54	0.1	4
Tricol Blackjack	Colombia Chemical	54	0.1	4

# Hex and Trivalent Black chromium



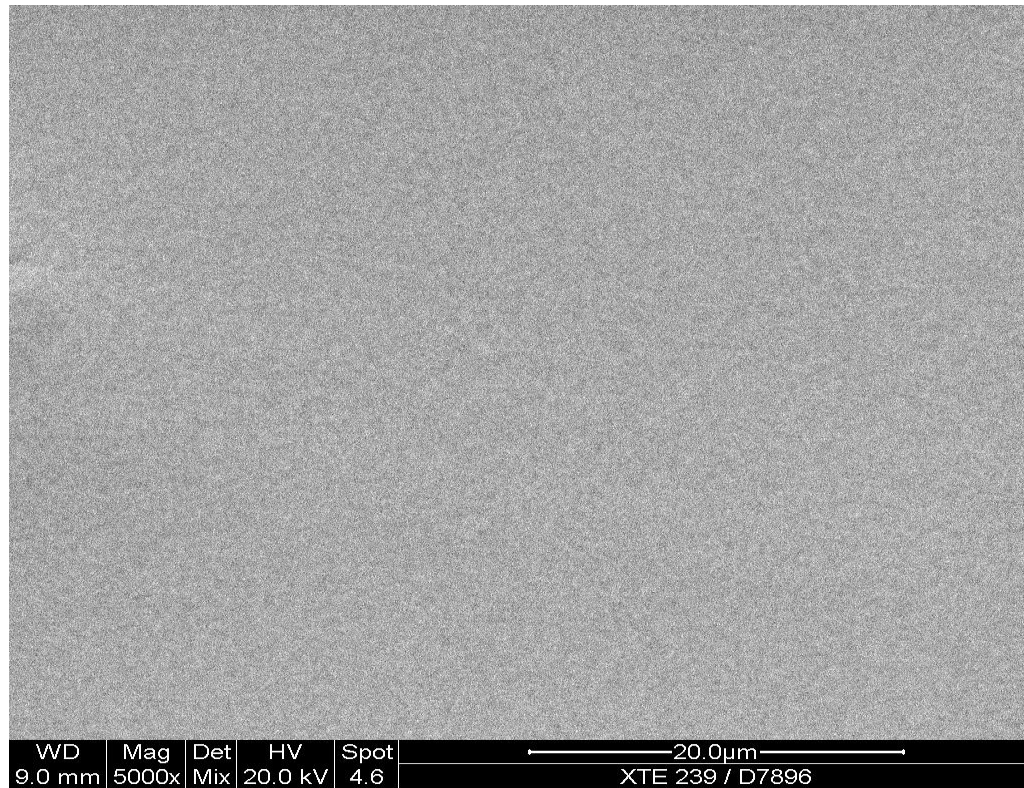
# Surface Scan

## Hexavalent Black chromium



# Surface Scan

## Trivalent Black chromium



# Deposit Structure

## Trivalent Black

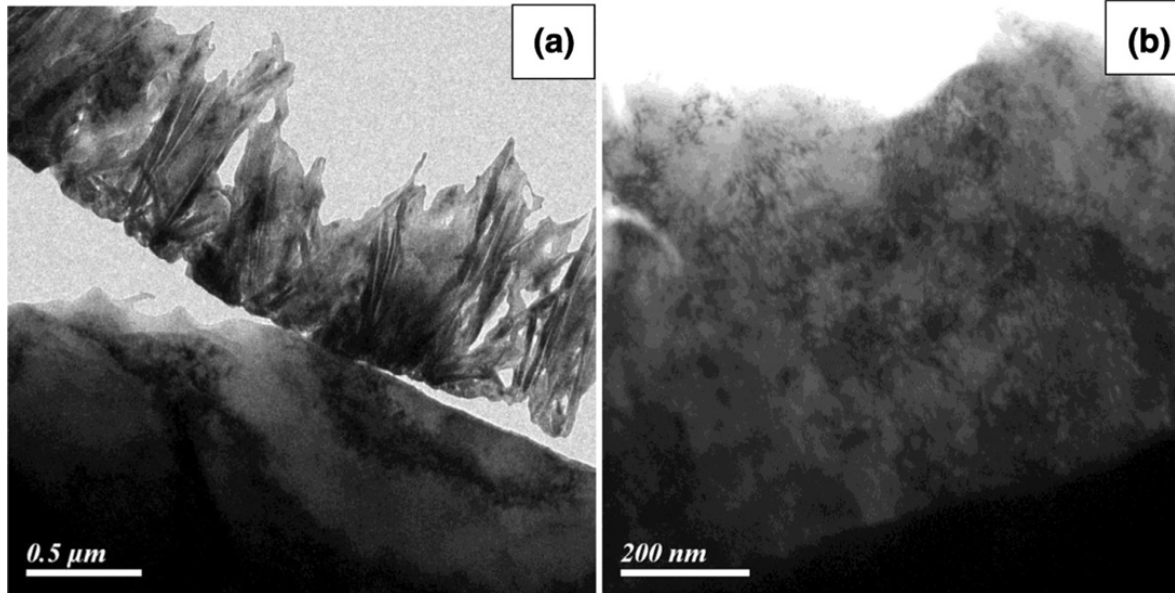
- Amorphous
- Glass-like
- Deposit can get cloudy at higher thicknesses

## Hexavalent Black

- Crystalline
- 50% chromium oxide / 50% chromium
- As-plated deposit can be non-uniform
- Post-treatment with waxes and oils can enhance the color and reflectivity



# TEM micrograph of trivalent black chromium coating



Chloride Electrolyte [4]

Sulfate Electrolyte [4]

Transmission Electron Microscopy – Showing structure and morphology

# Environmental Health and Safety

- Chromium (VI)
  - Toxicity is much greater
  - Classified as carcinogen
  - OSHA's Permissible Exposure Limit (PEL) for Cr (VI) is  $5\mu\text{g}/\text{m}^3$
  - Respirator and skin protection required
  - Use of ventilation, scrubber system, push air.
- Chromium (III)
  - Less toxic
  - No data on the carcinogenic potential
  - OSHA's Permissible Exposure Limit (PEL) for Cr (III) is  $500\mu\text{g}/\text{m}^3$
  - Skin protection required
  - With use of wetter, the system is regulated similar to nickels.

# Waste Water Treatment

- Hexavalent chromium significant WWT concern
- WWT process 3-step
  1. Reduce Cr(VI) to Cr (III) (w/sodium meta bisulfite) at low pH
  2. Raise pH 9-10 to form chromium hydroxide
  3. Precipitate and filter
- Trivalent chromium similar without first step
- Trivalent chromium also decreases chance of hexavalent chromium discharge

# Black chromium Applications:

- Motorcycle
- Automotive
- Consumer/Medical
- Industrial
- Solar Panels

# Motorcycle Applications



# Black Chromium Muffler Pipes



Photo courtesy of Calchromium



# Black Chromium Muffler Tips



Photo Courtesy of Polaris Industries



# Motorcycle Applications



Harley Davidson Black chromium Master Cylinder

[www.arlingtonplating.com](http://www.arlingtonplating.com)

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# Motorcycle Applications



Harley Davidson Brake Pedal



# Automotive Applications



“Cadillac adds black chromium package to spark CTS and ATS sales”

# Automotive Applications



Honda Accord Black chromium Grille Accent

# Automotive Rear Garnish



Honda Accord Rear Garnish



# Automotive Applications



Black chromium rear exhaust bezel – Honda Accord

[www.arlingtonplating.com](http://www.arlingtonplating.com)  
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# Automotive Wheel Rims





# Automotive Paddle Shifter



Cadillac ATS or CTS Magnesium  
Paddle Shifters

# Automotive Exhaust Tips



Jones Dual Oval Exhaust Tip



Lexus GX460 Exhaust Tip

# Consumer/Medical Applications



Ray Ban Sunglass Frames



Welch Allyn Otoscope

Photo's courtesy of Anoplate Corporation

# Industrial Applications – Black chromium

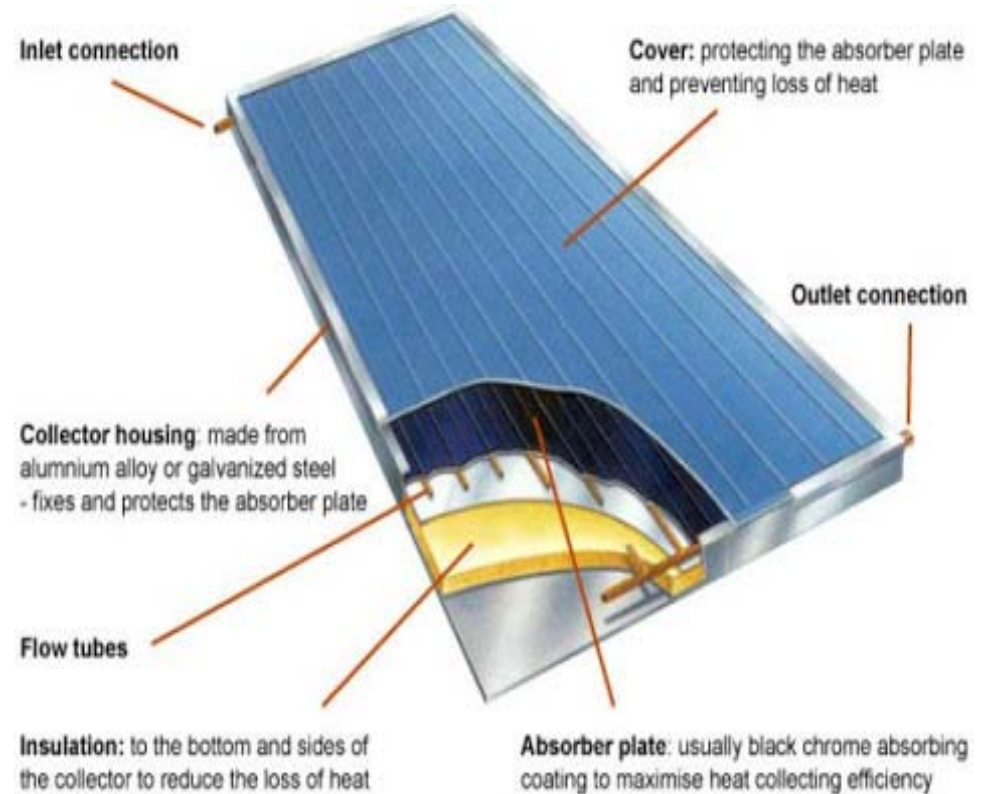


Linear motion guides



Color  
Uniformity  
Wear Protection

# Solar Applications – Black chromium



Black chromium absorbs and retains thermal energy



# Alternatives to black chromium:

- Black Anodizing
- Black Electroless Nickel
- Vapor Phase Deposition (PVD)
- Black Powder Coat
- Black Paint
- Black Oxide
- Black Chromate on Zinc
- Moly Black Electrolytic Nickel

# Summary

- The black color is more prominent today on motorcycles and automotive exterior trim
- Hexavalent black will provide the deepest black finish
- Hexavalent black will have the same OSHA exposure, operational, and environmental concerns as Hexavalent bright chromium
- New Trivalent blacks are darker and the color can be controlled with additives and filtration
- Trivalent blacks will operate similar to a watts nickel process with less environmental, health and safety concerns

# Thank you!

Questions?



# Sources:

- [1] Gilbert, L. O.; Buhman, C. C (1947) *US2623847A* Retrieved from <https://patents.google.com/patent/US2623847A>
- [2] Wilson, K. S. (1968) *US3602935A* Retrieved from <https://patents.google.com/patent/US3620935A>
- [3] Snyder, D. L. (2011). Decorative Chromium Plating. *Metal Finishing* 109 (11A), 177-187
- [4] Sheu, C et. Al (2015). Electrodeposition of black chromium–cobalt alloy based on trivalent sulfate electrolyte. *Journal of Taiwan Institute of Chemical Engineers*, 59 (2016), 496-505.
- [5] Agency of Toxic Substance and Disease Registry Case Studies in Environmental Medicine (CSEM), (2008).